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SOME EFFECTS OF VARIATION OF HOT-PRESSING TEMPERATURE UPON THE AGGLOMERATION OF MgO IN A DISPERSION STRENGTHENED NICKEL-MgO ALLOY

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SOME EFFECTS OF VARIATION OF HOT-PRESSING TEMPERATURE UPON THE AGGLOMERATION OF MgO IN A DISPERSION STRENGTHENED NICKEL-MgO ALLOY[1]

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SUMMARY

Agglomeration of oxides in a nickel-MgO composite was shown to increase with hot-pressing temperatures that ranged from 1800° to 2400° F and to be influenced by the presence of impurity oxides. The most encouraging result of this investigation was that the hot-pressing method seemed adaptable to producing a dispersoid in a metal matrix approaching dimensions in those of aluminum - aluminum oxide SAP-type alloys. The finest dispersions were obtained in extruded products by using the lowest hot-pressing temperature prior to extrusion and the finest metallic powders.

INTRODUCTION

In the decade since Irmann (ref. 1) published his work on the increased strength obtainable in aluminum by the addition of Al_2O_3 dispersoids, there have been many attempts to create strong, stable, dispersion-strengthened alloys from other metal-oxide systems. In general, however, properties of such artificially created materials have not, for the most part, come up to expectations. One of the reasons for this result, it is believed, is that the dispersions have not been fine enough.

One method used to obtain fine dispersions of oxides in a metal matrix is the method of mechanical mixing. It seems logical that, if a fine dispersion is desired and if oxide dispersoids are to be mixed in a metallic matrix utilizing powder metallurgy means, the finer the powders of both metal and oxides used, the more chance there would be to get a fine dispersion. The authors found evidence of this phenomenon in another

[1]Presented at the American Institute of Mining and Metallurgical Engineers Fall Meeting, Philadelphia, Oct. 17-21, 1960.

study (ref. 2), where, by ball milling to decrease the particle size of nickel powder, a fine dispersion of MgO in a nickel matrix was made. In the investigation reported herein, ball mills were used to reduce the size of, and to mix, metal and oxide powders.

Preliminary work at this laboratory showed that hot pressing produced finer dispersions than cold pressing and sintering. This is believed due to the fact that during hot pressing the compact was densified much more rapidly than during a sintering operation and thereby the oxide particles had much less time to grow. An example of the fine structures that were obtained by hot pressing in this preliminary work is shown in figure 1. The electron micrographs illustrate that the oxide dispersions produced in nickel were comparable with those in Al-Al_2O_3 sintered aluminum powder (SAP). Note that the particle sizes of oxide and interparticle spacings are comparable.

Preliminary work has also shown that the sintering temperature had a significant effect on agglomeration of oxide dispersoids during fabrication of this type of alloy. It was therefore anticipated that hot-pressing temperature could have a similar effect.

The objective of this study was to determine the effects of different hot-pressing temperatures and initial particle sizes of metallic powders on agglomeration of oxides and subsequently on the type of dispersion that can be obtained in a nickel-MgO dispersion alloy. A secondary objective of the study was to show some evidence relating to the effects of impurity oxide pickup on the gross agglomeration of the dispersoids.

Nickel powders of 2.5-, 1.0-, and 0.2-micron average particle size were used for this investigation. The 1.0- and 0.2-micron powders were combined with 20 volume percent of 0.05-micron average particle size MgO. The powders were variously vacuum-hot-pressed at temperatures of 1800°, 2100°, and 2400° F and then extruded at 2300° F at a reduction ratio of 16 to 1. The specimens were examined by optical microscopy to determine the mean free path of the dispersions.

MATERIALS, APPARATUS, AND PROCEDURE

Specimens for this investigation were prepared from nickel and MgO powders by grinding, mixing, washing, drying, hydrogen cleaning, cold packing, and vacuum hot pressing of the powders with subsequent canning and extrusion of the hot-pressed billets. The specimens, so prepared, are listed in table I.

The starting materials used in this study were International Nickel Co. Carbonyl "B" nickel powder of 2.5-micron average particle size (Fisher Sub-Sieve Sizer average particle size) and Baker's magnesium

oxide, reagent grade, of 2-micron average particle size. All subsequent particle sizes reported are those obtained in the Fisher Sub-Sieve Sizer except where noted.

The powders were processed as illustrated in figures 2 and 3. The powders used to produce the extrusions with no oxide additions were not ground. The nickel powders for all other specimens, 3 to 8, were ground in a Szegvari Attritor Mill with n-heptane and 2 percent oleic acid[2] for 10 or 72 hours, depending on whether 1.0- or 0.2-micron powder was desired, respectively. Five hours prior to the end of the grinding runs, 115 grams of magnesium oxide, which had been preground to 0.05 micron (as determined by B.E.T. analysis) in n-heptane with 2 percent oleic acid, was added and mixed with the nickel powders. The initial grinding charge in a 1-gallon attritor mill for each run was 1100 grams of nickel powder, 25 grams of oleic acid, 1400 milliliters of n-heptane, and 10 kilograms of 1/8-inch stainless steel balls. n-Heptane was added to the mill throughout the run to keep the slurry just thin enough so that it would run off a spatula.

All the powders except those for billet 1 were subsequently cleaned in purified hydrogen at 650° F for 5 hours. The powders were then pressed by hand into graphite dies in a controlled atmosphere of argon. Billets 1 and 2 were vacuum-hot-pressed at a pressure of 5000 psi at 2100° F for 1 hour. Billets 3 and 6, 4 and 7, 5 and 8 were vacuum-hot-pressed at a pressure of 4500 psi at 1800°, 2100°, and 2400° F, respectively, for 1 hour. Prior to heating, the vacuum chamber was evacuated to a pressure of about 0.5 micron. After hot pressing, the billets were canned in mild steel and subsequently extruded at 2300° F at a ratio of 16 to 1.

It should be noted that, in spite of the reasonable precautions that were taken to avoid oxygen pickup in the powders, there were many chances for oxidation. The significance of this is discussed later.

RESULTS AND DISCUSSION

The densities of hot-pressed and extruded specimens are shown in table I. The specimens (1 and 2) made from the original 2.5-micron nickel powder, without oxide addition, that were utilized as a basis for comparison had relatively high densities of over 99 percent in the hot-pressed condition. Nickel powders of 0.2-micron particle size, to which 20 volume percent of MgO had been added, exhibited a low density of 82 percent for the specimen hot-pressed at 1800° F (specimen 3) and greater

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[2]Weight percentage oleic acid was determined by considering only the weight of oleic acid and powder to be ground as the charge.

densities for specimens hot-pressed at 2100° and 2400° F (specimens 4 and 5). In those specimens made from 1-micron nickel powders plus MgO, the specimen hot-pressed at 1800° F again exhibited a low density of less than 82 percent (specimen 6), while the specimen hot-pressed at 2400° F had 100-percent density in the as-hot-pressed condition. The data also show that the extrusion process has further densified the specimens, which in some cases had a high degree of porosity in the as-hot-pressed condition.

Figure 4 shows measurements of mean free paths of oxide dispersoids in the nickel matrix for two different sizes of nickel powders and for both the hot-pressed and extruded conditions. These measurements were made on optical photomicrographs taken at a magnification of X2000. The number of particles intercepted per unit length of random line through the photograph, N_L, was determined. Mean free path then equals $(1 - f)/N_L$ (ref. 3), where f equals the volume fraction of oxide that was assumed to be 20 percent, the amount of MgO added. In the case of the hot-pressed specimens, the mean free paths that were measured show a general increase with increasing hot-pressing temperature. Actually, the measurements that were made of the hot-pressed billets (values shown in fig. 4) were made of the surfaces rather than the interiors of the specimens. (The measurements were made on chips that were machined from the surfaces.) It is shown later that the values obtained from the surface of the hot-pressed billets are not a true measure of the fineness of the dispersion in the interior of the hot-pressed billets, and thus it must not be assumed that differences between the observed structures in the hot-pressed billets and the extruded billets are caused by the extrusion process.

In the case of the extruded specimens, the mean free paths show a relation to the hot-pressing temperatures utilized prior to extrusion in that they increased (for the most part) as the hot-pressing temperature was increased. In both hot-pressed and extruded specimens mean free paths increased with increasing hot-pressing temperature as a result, of course, of growth of the larger and disappearance of the smaller oxide particles.

Figure 4 shows that finer dispersions of oxides (smaller mean free paths) were obtained when the finer nickel powders were used. The best distribution that was measured in the specimens occurred in the surface of the specimen made from 0.2-micron nickel powder and hot-pressed at 1800° F. This specimen had a mean free path of 0.6 micron.

The sizes of the dispersoids in the extruded products were very large relative to the observed particle sizes in the surface of the hot-pressed specimens and, in fact, the "indicated" agglomeration of particles was much greater than that expected. Metallographic comparisons of the microstructure showed that, in some cases, the indicated agglomerations

were so great that they would have effectively destroyed the potential mechanical properties of the product. An example of such an "indicated" agglomeration is shown in figure 5 by a comparison of the structure of an extruded specimen and the surface structure of the hot-pressed billet from which the extrusion had been made. At this point, the fact that the microstructures of the hot-pressed specimens were not representative of the true structures of the materials had not been realized. As studies of the structures progressed, the skin structure upon which the measurements were made was found to be different from the interior structure of the as-sintered billets, as will be shown. However, since the initial billets from which the metallographic samples were obtained had been extruded, it was impossible to study the interiors of the original billets in the as-sintered condition.

In another study being conducted simultaneously with the present investigation, further indications of agglomeration problems were observed. Here, quantitative measurements of the microstructures of specimens of extruded products showed a considerable increase in the quantities of oxide dispersoids over that anticipated from the known volume percent of oxide added to the material. It was concluded from such measurements that, in spite of the attempts made to keep the powder clean and to reduce surface oxides from the powder during the fabricating practice, impurity oxides were being picked up somewhere in the fabricating practice.

To answer questions pertaining to the different programs being conducted (including questions raised in the present investigation), additional billets were made up on a smaller scale in a vacuum hot-pressing chamber for study of the hot-pressed and the hot-pressed and heat-treated microstructures. Hot pressing was done at a temperature of 2100° F, as were the heat treatments. Incidentally, the original billets used for the main part of this investigation were hot-pressed at one commercial laboratory and extruded at another commercial laboratory. Although precautions were taken in the handling and packaging of these products, it is most difficult to maintain or to prevent impurity pickup in products that are shipped to different areas for processing, no matter how much care is utilized. The simulated billets and heat treatments used, subsequent to the initial process, showed what is believed to be a true representation of the problems of agglomeration in the original hot-pressed products. For example, a billet that had been prepared in a manner similar to that of specimen 4 of this investigation (hot-pressed at 2100° F for 1 hr at 4500 psi) was examined to determine the gross structure of the billets. Figure 6 shows that there were differences in the structures at the surface and in the interior of the billet. On a macroscale, the skin looked similar to a partially decarburized zone in a steel. It is notable that the surface had a finer dispersion than the interior. Thus, a reduction of oxide (undoubtedly nickel oxide) at the surface of these billets probably occurred because of the proximity of such oxides to the graphite of the hot-pressing dies, the MgO, of course, remaining

in unreduced form. Such a partially deoxidized zone would indirectly indicate either that oxygen was picked up in the specimens during the handling of the powders or that it had never been completely removed during the cleaning of the powders.

Another opportunity for the structure to have agglomerated occurred during the extrusion practice. It was necessary to soak the original full-sized billets prior to extrusion; the billets were soaked for 2 hours at the extrusion temperature. The specimens of this investigation were soaked at 2300° F for 2 hours and extruded at 2300° F. A simulated billet that had been prepared in a manner similar to that of specimen 4 of this study was given an additional furnace treatment or heat treatment of 2 hours at 2100° F. Figure 7 compares the microstructure of the interior of this billet in the hot-pressed condition and after annealing for 2 hours at 2100° F. It is evident that heat treating significantly increased the agglomeration of the oxides in the specimen relative to those of the as-hot-pressed material. If the specimen had been heat-treated at 2300° F, at the temperature at which the specimens of this study were extruded and presoaked, agglomeration probably would be even greater than that shown in the figure. In further work with these types of powders, chemical and microstructural analyses of pure nickel specimens showed that up to 2 weight percent oxygen was picked up in the handling of the powders. Also, the hydrogen cleaning operations did not remove all the nickel oxide from the specimens.

From the preceding evidence and from studies of the skins of hot-pressed billets, it was concluded that nickel oxide was present in relatively large amounts in the products, and it is postulated that this nickel oxide in the composite affects the dispersions by promoting agglomerations of the MgO-NiO in these alloys. Other experiments corroborate this conclusion. Several specimens ball-milled to different sizes and cleaned in hydrogen were made from nickel powders alone. Microstructural studies of such specimens revealed visually a differing amount of impurity nickel oxide in the specimens; this impurity increased as the particle sizes were decreased. A photomicrograph of one of these specimens is shown in reference 2. Finally, in recent studies of agglomeration made at this laboratory, longtime heat treatments at 2300° F of MgO dispersoids in highly purified nickel did not show appreciable agglomeration.

Regardless of the portion or portions of the fabricating phase that produced the agglomeration, it is believed that the nickel oxide definitely facilitated the process of agglomeration. Its presence in the matrix as individual particles of NiO or as attached coatings adjacent to MgO particles (since the NiO-MgO oxides are mutually soluble on each other) would tend to promote agglomeration. The nickel oxide alone, being unstable, would dissociate and could essentially seed upon other oxides. Distances between oxide particles, whether they are pure or impure MgO or MgO-NiO solid solutions, would be less; and thus diffusion

could occur in short time periods. It is also probable that surface-energy effects could be active, since many of the NiO particles could be present in small sizes relative to the size of MgO added deliberately. Another contributing fact could be that the combined solid solutions of the NiO-MgO could have a lower stability or less negative free energy than would pure MgO in a nickel matrix. Finally, the fact that an increase in the effective oxide content could also increase the agglomeration should not be ignored (ref. 2). Many of these phenomena are discussed on a more fundamental basis in the paper by Cochardt (ref. 4).

Considering, then, that the oxides observed in the microstructures may have in part been combined with MgO or may in some cases be individual particles of NiO, the microstructures of the extruded composite materials are of great interest (see fig. 8). It may be noted that the 1-micron nickel powder specimens had a greater change in the dispersion with different hot-pressing temperatures than did the specimens from 0.2-micron nickel powder. Such measurements agreed with a mean free path measurement for the extruded specimens shown in figure 4. This difference could be related to impurity contents of the specimens; the material made of finer powdered metals is believed, from microstructural studies, to contain more impurities. The effect of this greater amount of impurity in the specimens prepared from finer powdered metals might be to mask the effect due to the different hot-pressing temperatures. In the materials prepared from the coarser powdered metals, temperature might play a more significant role because the impurity content is not high enough to cause a great amount of agglomeration at the lower temperatures. Other factors, however, could have accounted for the differences in agglomeration, but these are not known as a result of these studies.

It is also interesting to note that the interparticle spacings at the edges of the 1800° F hot-pressed specimens approximated those of sintered aluminum powder products (0.4-micron interparticle spacings as noted in ref. 5); and in fact, even with impurities and agglomeration, the specimen hot-pressed at 1800° F and extruded had a reasonably fine dispersion of 1.6 microns. Certainly, with still greater processing and cleaning care, the dispersions of MgO in nickel should be considerably better. Such work is underway at the present time.

CONCLUDING REMARKS

In summary, the agglomeration of an MgO dispersion in a nickel matrix increased with increasing hot-pressing temperature during a vacuum hot-pressing operation. Also, when 0.2-micron nickel powder was used as a starting material, finer dispersions were obtained than when a coarser, 1-micron nickel powder was used. The finest dispersions were obtained by using the lowest hot-pressing temperature and the finest metallic powders. The mean free path of this dispersion after hot pressing was 0.6 micron

in the surface of the hot-pressed billet. Finally, mean free paths increased, generally, with hot-pressing temperature as a result, of course, of growth of the larger and disappearance of the smaller oxide particles.

Perhaps the most encouraging result of this investigation was the fact that the hot-pressing method seems adaptable to producing a dispersoid in a metal matrix approaching in dimension those of Al-Al_2O_3 SAP-type alloys. These fine dispersoids were obtained by using metallic particles that were no smaller than 0.2 micron. Perhaps to get an analogy exactly equivalent to that of SAP it may not be necessary to use metal powders finer than 0.1- to 0.2-micron average particle size.

Finally, the indirect evidence of the effect of impurity NiO on the possible agglomeration of the gross oxide products in the composites of this study has very practical connotations. The presence of any impurity oxides in a dispersion-strengthened product may prove to lower effectively the stability of the dispersoids and the matrix to such a degree that the full SAP potential of a product cannot be attained. Certainly, considerable effort must be undertaken to prevent the pickup or retainment of impurity oxides, presuming that the matrix of the dispersion-strengthened product is not alloyed and does not have agents which, in themselves, would tie up or reduce the residual or impurity oxides.

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National Aeronautics and Space Administration
Cleveland, Ohio, September 21, 1961

REFERENCES

1. Irmann, R.: SAP - A New Material of the Powder Metallurgy of Aluminum. Tech. Rundschau (Bern), no. 36, 1949, pp. 19-26. (See also WADC TR-414, July 1959, p. 140.)

2. Schafer, Robert J., Quatinetz, Max, and Weeton, John W.: Strength and High-Temperature Stability of Dispersion Strengthened Nickel-MgO Alloys. Trans. AIME, vol. 221, Dec. 1961, pp. 1029-1104.

3. Fullman, R. L.: Measurement of Particle Sizes in Opaque Bodies. Trans. AIME, vol. 197, 1953, pp. 447-452.

4. Cochardt, A. W.: Some Estimates of the Thermal Stability of Dispersion-Hardened Alloys. Trans. AIME, vol. 209, Apr. 1957, pp. 434-437.

5. Irmann, R., von Zeerleder, A., and Rohner, F.: SAP - Properties of Warmpressed Sintered Bodies of Aluminum Powder. Festschrift Prof. Mirko Ros, Schweizer Archiv f. Angewandte Wissenschaft u. Technik, Verlag Solothurn, 1950. (See also WADC TR-414, July 1959, p. 36.)

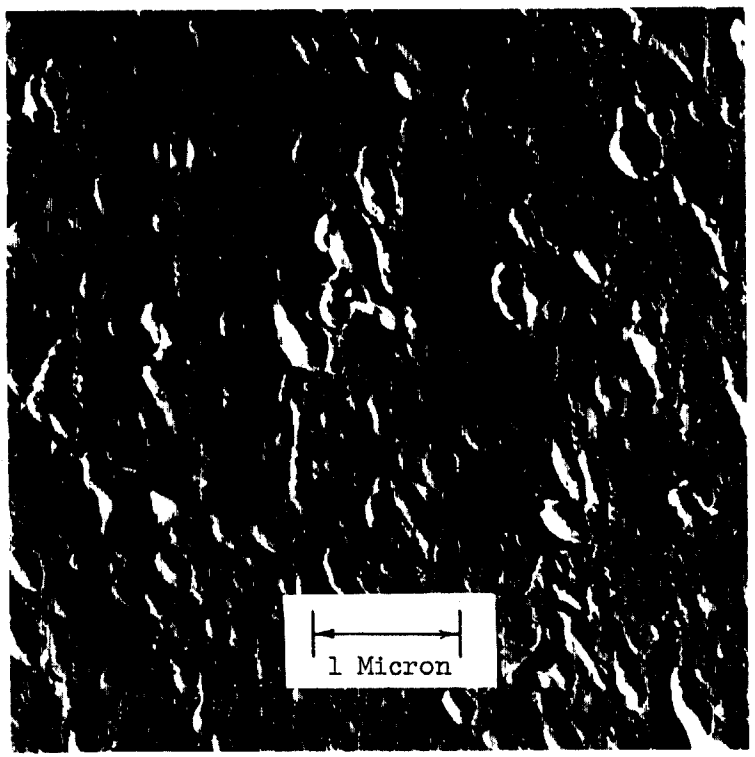
TABLE I. - FABRICATION CONDITIONS AND DENSITIES OF HOT-PRESSED AND EXTRUDED Ni AND Ni-MgO ALLOYS

Specimen	Size Ni powders, microns	Volume percent MgO (a)	Hot pressing		Density, percent theoretical	
			Temperature, °F (b)	Pressure, psi	As hot-pressed	As extruded (c)
1	2.5	None	2100	5000	99.3	100.0
2			2100	5000	99.0	100.0
3	0.2	20	1800	4500	82.0	97.1
4			2100	4500	95.0	98.1
5			2400	4500	93.0	97.6
6	1.0	20	1800	4500	<82	98.8
7			2100	4500	92.1	97.0
8			2400	4500	100.0	98.9

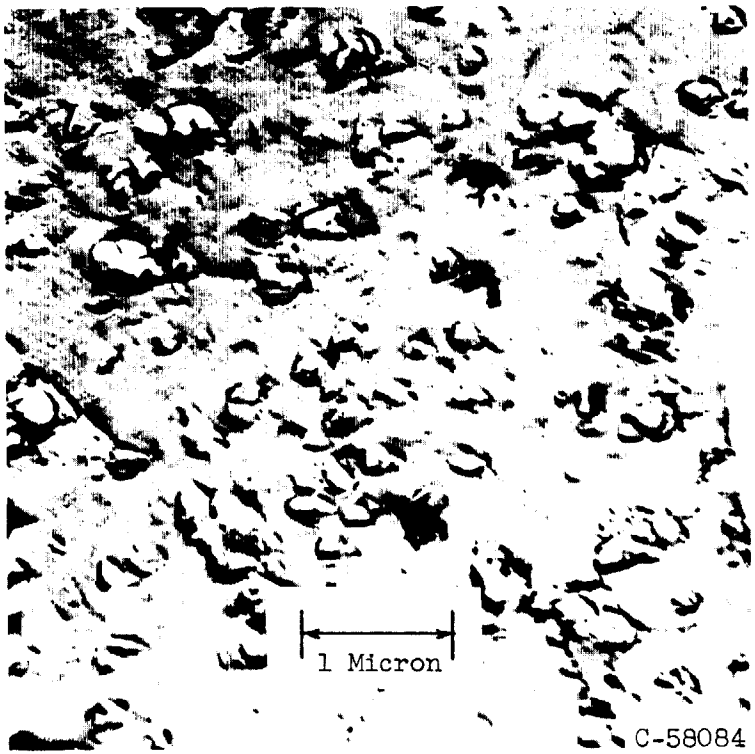
[a]MgO particle size, 0.05 micron.

[b]Hot-pressing time at temperature, 1 hour.

[c]Extrusion temperature, 2300° F; reduction ratio, 16 to 1.



(a) Dispersion of Al_2O_3 in Ni.



(b) SAP dispersion-strengthened aluminum.

Figure 1. - Comparison of an Al-Al_2O_3 SAP structure with a Ni-Al_2O_3 dispersion prepared by mechanical mixing techniques. X20,000.

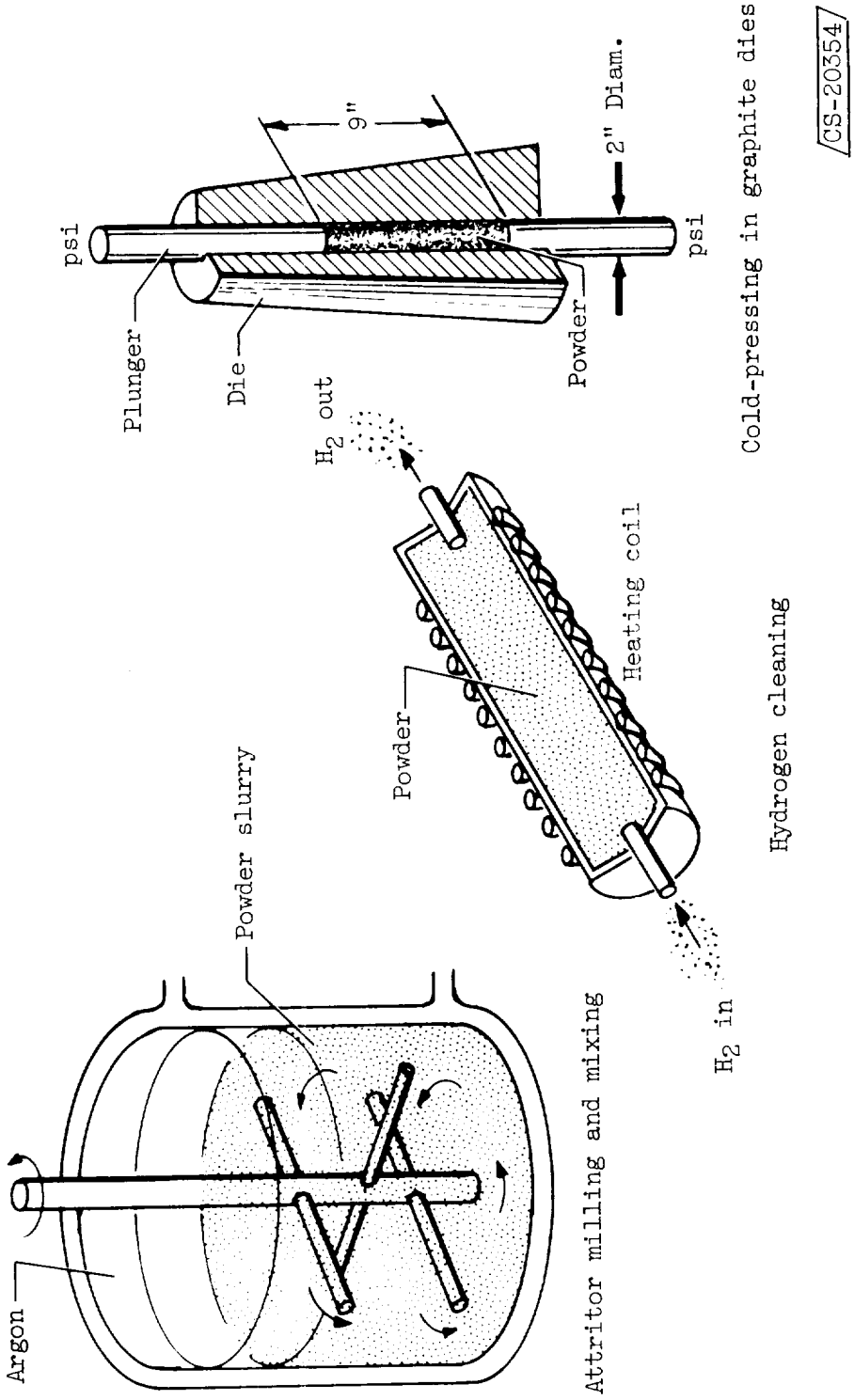


Figure 2. - Processing of Ni-MgO composites.

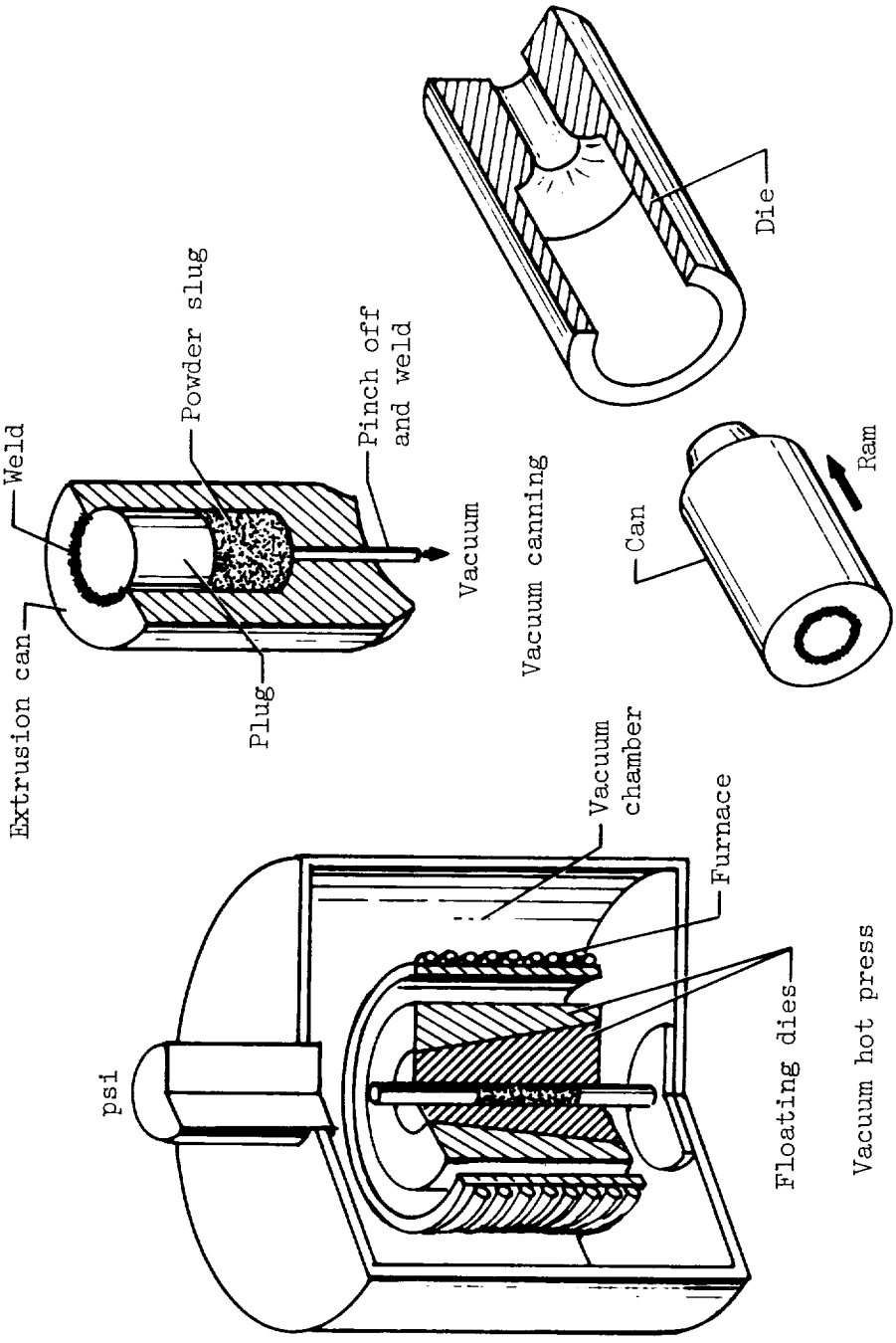
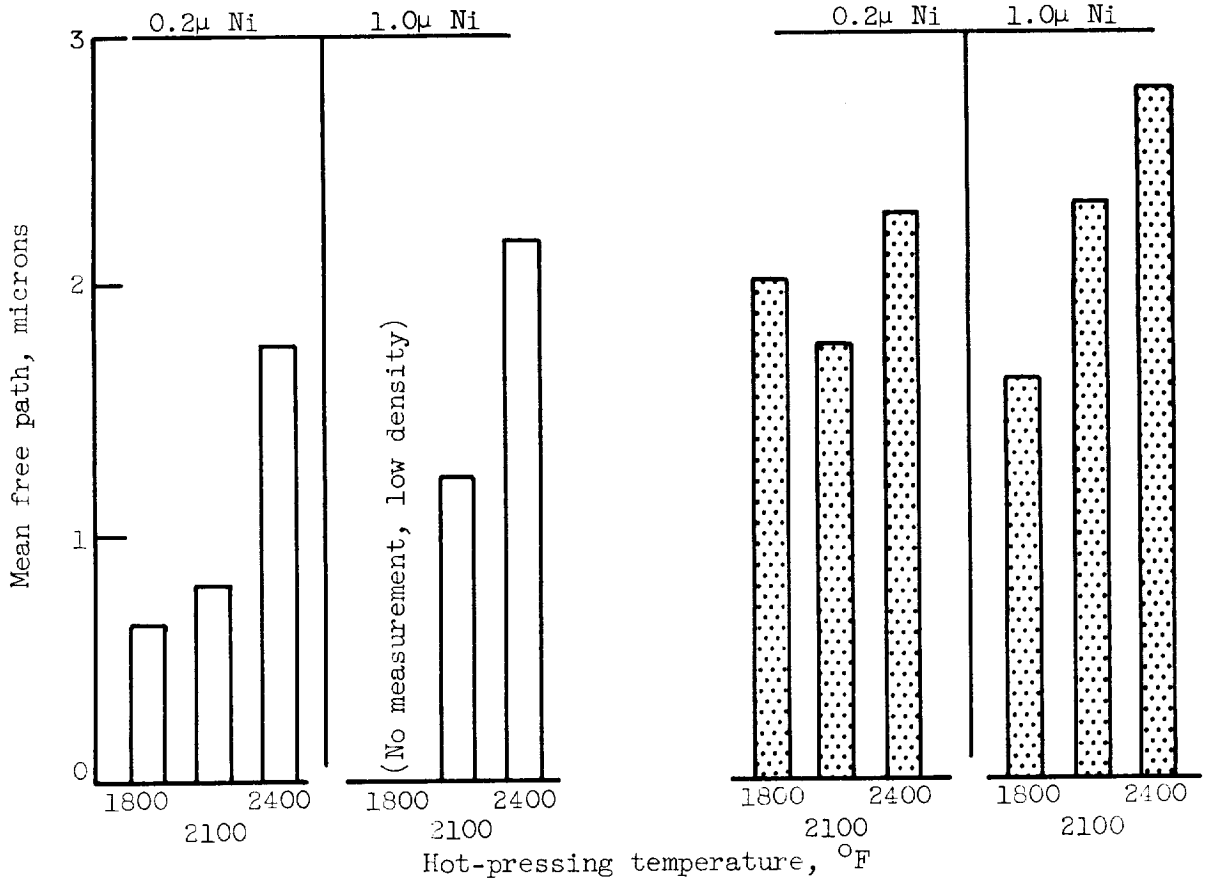


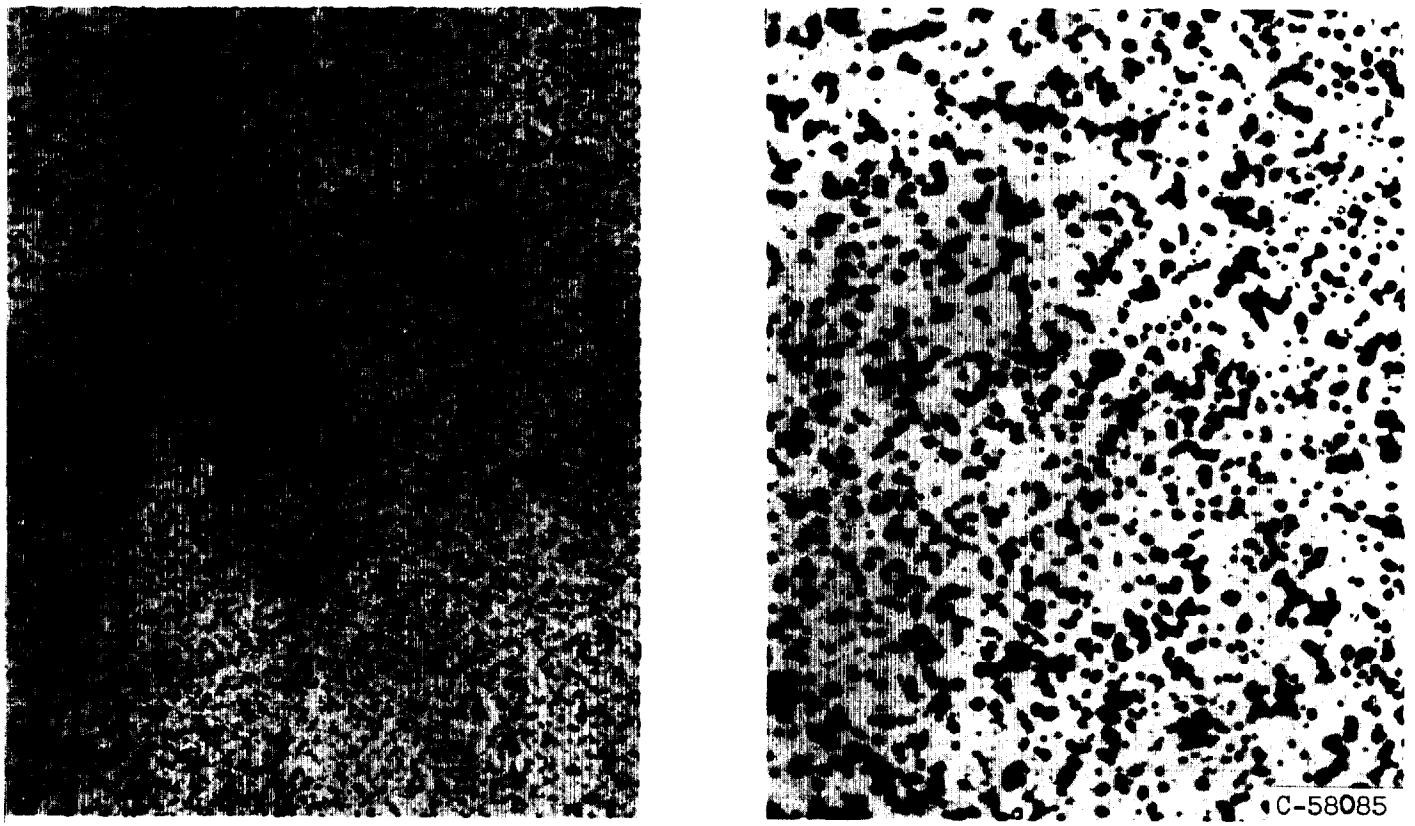
Figure 3. - Processing of Ni-MgO composites.



(a) Hot-pressed specimens (near surface of billet).

(b) Extruded specimens (interior of billet).

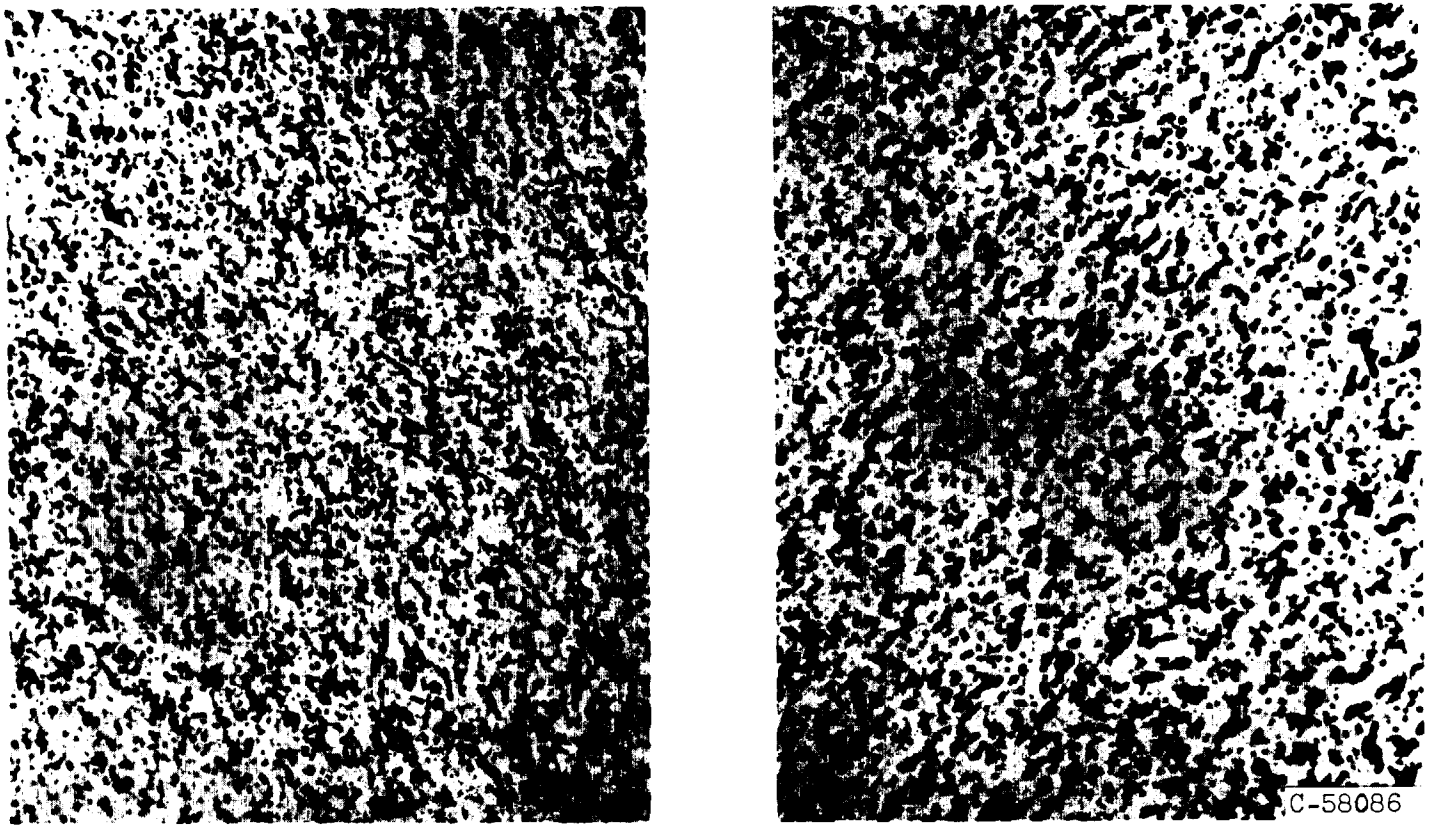
Figure 4. - Relations between mean free path and hot-pressing temperature.



(a) Hot pressed at 1800° F (surface of billet).

(b) Hot pressed at 1800° F and extruded at 2300° F.

Figure 5. - Maximum oxide agglomeration observed between surface of hot-pressed specimen and interior of same specimen after extruding. Unetched; X2000.



(a) Near surface of billet.

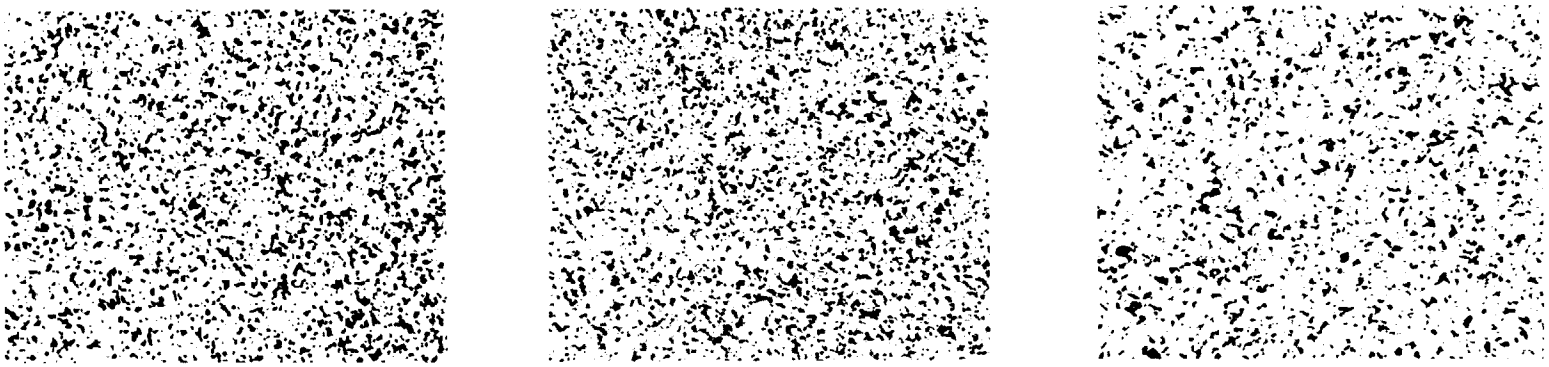
(b) Interior of billet.

Figure 6. - Differences in dispersoid size between surface and interior of billet hot-pressed at 2100° F in graphite dies. Unetched; X1000.

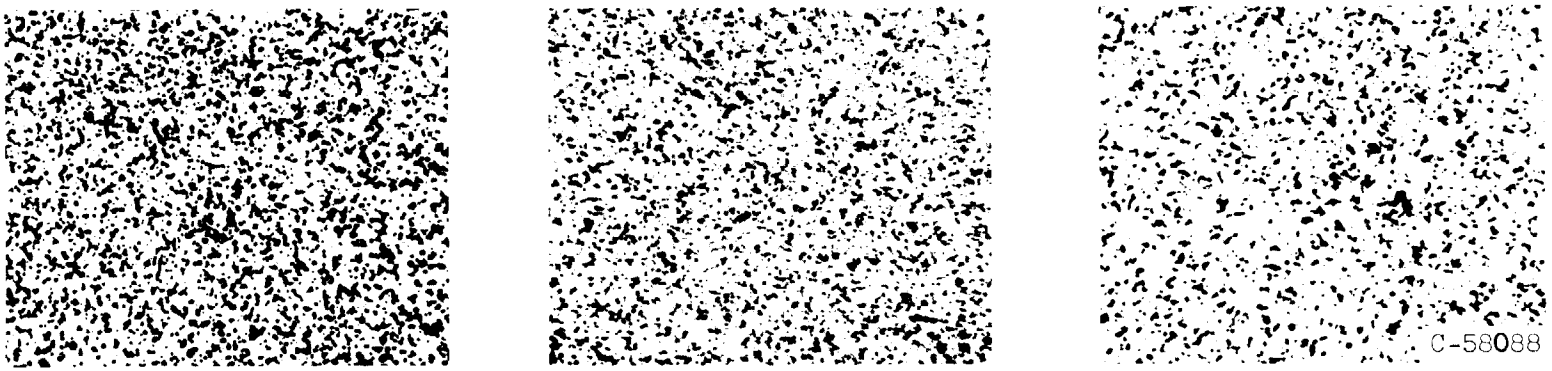
(a) Hot-pressed at 2100° F for 1 hour.

(b) Hot-pressed at 2100° F for 1 hour and annealed at 2100° F for 2 hours.

Figure 7. - Differences in dispersoid size between hot-pressed and hot-pressed-and-annealed billets. Unetched; X1000.



(a) 0.2μ Ni.



1800 2100 2400

Hot-pressing temperature, °F

(b) 1.0μ Ni.

Figure 8. - Effect of hot-pressing temperature and matrix particle size on degree of agglomeration. Unetched; X1000; extrusion temperature, 2300° F.